

Ab-initio calculation method for charged slab systems using field-induced gaussian sheet

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A new repeated-slab calculation method is developed to simulate the electronic structures of charged surfaces by arranging density-variable charged sheets in vacuum regions to realize a constant potential on the charged sheets and maintain the charge neutrality condition. The charged sheets are fabricated so as to screen an electric field from charged slabs; consequently, they act like a counter electrode composed of flat perfect conductors, modeling a tip of a scanning tunneling microscope or a reference electrode in an electrochemical cell. This method has the advantages of ease of implementation into existing repeated-slab programs and low computational costs. The availability of the method is demonstrated by applying it to a charged H₂ molecule and charged Al(111) metal and Si(111) semiconductor surfaces.

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I. INTRODUCTION

A surface becomes an interesting stage for material transformations such as chemical reactions when the surface is placed under an external electric field and has positive/negative charges. In the scanning tunneling microscope (STM), for example, the applied sample bias produces an electric field between the surface and the STM tip.¹ Such electric field often induces a variety of surface reconstructions,² desorption,³ and the diffusion/rotation of adsorbates.^{4,5} On the other hand, in electrochemistry, the manipulation of electric fields is a key factor in controlling chemical reactions.^{6,7}

Ab-initio calculation using a repeated slab has greatly contributed to the exploration of the geometric and electronic structures of a number of surfaces. Such calculation employs a periodic boundary condition (PBC) perpendicular to the slab; thus, it receives the benefit of numerous computational techniques developed in the calculations of periodic bulk systems. However, most of these calculations are concerned with neutral surfaces, because various physical quantities such as energy and potential diverge to infinity unless charge neutrality is maintained within a unit cell in an electronic structure calculation based on the PBC scheme.⁸

To treat charge-neutral surfaces in an external electric field, Neugebauer and Scheffler⁹ introduced artificial dipole sheets in vacuum regions of a repeated unit cell. Arranging the positive and negative charged sheets on the front and back sides of the slab, respectively, one can easily impose a constant electric field on the slab system. The calculation method for a charged slab was performed by Fu and Ho.¹⁰ In their method, artificially charged sheets, which have the same amount but an opposite sign of charge to that of the slab, are placed on both sides of the slab. These artificially charged sheets

terminate the electric field originating from the charged slab. All these computational recipes dexterously realize the charge neutrality and compensate the electric field in a unit cell, and they have been utilized in several studies for the elucidation of field effects on surfaces.^{11,12,13,14}

However, since these methods use sheets with fixed charge distributions, typically of plane Gaussian form, the electric field from a charged slab is in general not perpendicular to the sheet and the potential shows a modulation along the sheet. This feature becomes marked and produces some inconvenience when the surface of the slab is bumpy and the excess-charge distribution on the slab is far from uniform. For example, unless the thickness of the vacuum region is sufficiently large, the potential modulation on the sheet often produces unnecessary electrostatic interactions between repeated slabs, which makes it complicated to analyze the energetics on the slab. Furthermore, in the case of a STM experiment or an electrochemical cell, since a STM tip and a reference electrode are normally made of conducting materials, they have a constant potential but a nonuniform charge distribution, rather than a fixed uniform charge distribution (see Fig. 1(a)). To simulate the situations in which such a counter conducting material approaches a surface, it is desirable to adopt another calculational recipe using constant-potential charged sheets.

Recently, Otani and Sugino¹⁵ have developed a general method of simulating charged surfaces surrounded by screening mediums. They ingeniously combined a repeated-slab calculation with a real-space potential calculation to respond to any non-PBCs by releasing the charge-neutrality constraint of a unit cell. However, their method needs the regeneration of a potential in real space and requires additional computational costs.

The purpose of this work is to demonstrate a new computational recipe for simulating a charged surface lo-

cated near a counter metallic electrode maintaining the charge-neutrality constraint by only inserting a constant-potential charged sheet within the repeated-slab scheme. Our approach provides the advantages of ease of implementation into existing ab-initio calculation programs based on PBC and low additional computational costs for the charged slab calculation. The rest of this paper is organized as follows: in §II, we explain how to construct a constant-potential charged sheet and then present formulas to realize it using an existing ab-initio calculation program. In §III, we demonstrate how the present method works, by showing results for a charged H_2 molecule, charged Al(111) and Si(111) surfaces near an electrode. An attention with respect to the width of charged sheets is also presented. We give a brief summary of this paper in §IV.

II. FORMALISM

In this section, we consider how to construct a charged sheet that has a constant potential on the sheet. When one connects a conducting material and a surface with an electric battery, counter charge is induced on the conducting material by an electric field from the charged surface, and this realizes a constant potential on a conducting material, as shown in Fig. 1(a).¹⁶ To construct the induced counter charge, we first obtain the electric field from a charged slab.

We prepare an open space that is periodic in both x and y directions but nonperiodic in z direction, where the x , y and z directions correspond to the surface lateral and normal directions, respectively. The range of the z direction is limited to $0 \leq z \leq 2L$, and the center of the charged slab is located at $z = L$, as shown in Fig. 1(b). We assume that the slab has reflection symmetry at $z = L$, for simplicity. The charged slab produces an electric field outside the slab, *i.e.*, in the vacuum regions. The z component of such an electric field at the boundaries, $z^* = 0$ or $z^* = 2L$, is obtained as

$$E_z(z^*, \mathbf{g}) = - \int_0^{2L} \partial_z G(z = z^*, z', \mathbf{g}) \rho_{slb}(z', \mathbf{g}) dz', \quad (1)$$

where we performed a Fourier transformation along the $x - y$ direction and used the reciprocal component, \mathbf{g} . $\rho_{slb}(z, \mathbf{g})$ is the electronic density of electrons and ions in the slab region. $G(z, z', \mathbf{g})$ is the propagating Green's function obtained by solving the Fourier-transformed Poisson equation, $(\partial_z^2 - g^2)G(z, z', \mathbf{g}) = -4\pi\delta(z - z')$, where $g = |\mathbf{g}|$. If we set the electronic potential to zero at the cell boundaries, $G(z = z^*, z', \mathbf{g}) = 0$, this Green's function can be expressed as

$$G(z, z', \mathbf{g}) = \frac{2\pi}{g} e^{-g|z-z'|} + \frac{2\pi}{g} \times \frac{e^{-2Lg} \cosh(g(z-z')) - \cosh(g(z+z'-2L))}{\sinh(2Lg)}. \quad (2)$$

Then, we arrange the charged sheets at the boundaries, $z^* = 0$ and $z^* = 2L$. If the charge density on the sheet is determined so as to compensate $E_z(z^*, \mathbf{g})$, a constant potential is realized at the cell boundaries and the charge neutrality is naturally satisfied in $0 \leq z \leq 2L$ on the basis of Gauss's theorem. Therefore, we employ $E_z(z^*, \mathbf{g})$ to determine the charge densities on the sheets and adopt the half-Gaussian forms for the charge distribution along the z direction.

Since the above-mentioned cell, which is composed of the charged slab and counter charged sheets at the cell boundaries, is neutral and produces no electric field outside the cell, we stack such cells periodically along the z direction. In this case, the repeated counter charge density, $\rho_F(z, \mathbf{g})$, is given by

$$\begin{aligned} \rho_F(z, \mathbf{g}) = & - \frac{E_z(z^* = 2L, \mathbf{g})}{4\pi A} \\ & \times \sum_{n=-\infty}^{\infty} e^{-\left(\frac{z-2L(n+1)}{a}\right)^2} \theta(2L(n+1) - z) \\ & + \frac{E_z(z^* = 0, \mathbf{g})}{4\pi A} \\ & \times \sum_{n=-\infty}^{\infty} e^{-\left(\frac{z-2Ln}{a}\right)^2} \theta(z - 2nL), \end{aligned} \quad (3)$$

where θ and a are the step function and the width of a Gaussian charge, respectively. A is a normalization constant of a half-Gaussian distribution, $A \equiv \int_0^\infty e^{-\left(\frac{z}{a}\right)^2} dz = \frac{\sqrt{\pi}}{2} a$. Inserting eqs. (1) and (2) into eq. (3) and Fourier-transforming the result along the z direction, we obtain for $g \neq 0$

$$\begin{aligned} \rho_F(k, \mathbf{g}) = & -e^{-\left(\frac{ka}{2}\right)^2} \frac{g}{4\pi L} \tanh(Lg) \sum_{k'} \phi_{slb}(k', \mathbf{g}) \\ & - \frac{1}{4\pi L} \text{sgn}(k) \text{erf}(|k|a/2) \sum_{k'} \phi_{slb}(k', \mathbf{g}) k', \end{aligned} \quad (4)$$

and for $g = 0$

$$\begin{aligned} \rho_F(k, \mathbf{g} = \mathbf{0}) = & -e^{-\left(\frac{ka}{2}\right)^2} n_0 \\ & - \frac{\text{sgn}(k) \text{erf}(\frac{|k|a}{2})}{4\pi L} \sum_{k' \neq 0} \phi_{slb}(k', \mathbf{g} = \mathbf{0}) k', \end{aligned} \quad (5)$$

where k is the reciprocal component along the z direction and $\phi_{slb}(k, \mathbf{g})$ is the Coulomb potential due to the slab charge, $4\pi \frac{\rho_{slb}(k, \mathbf{g})}{k^2 + g^2}$. n_0 represents the excess electron number in a slab given by $n_0 = \int_{unit} \rho_{slb}(\mathbf{r}) d\mathbf{r}$. Positive and negative n_0 's correspond to an excess and a deficiency of electrons in the slab, respectively. Hereafter, we call this type of counter charged sheet a “field-induced Gaussian-charge (FIGC) sheet”.

In the repeated-slab calculation, the total charge density is obtained as the sum of the charge density of the FIGC sheet, $\rho_F(k, \mathbf{g})$, and that of the slab, $\rho_{slb}(k, \mathbf{g})$. Such a sum enables the electronic-structure calculation of

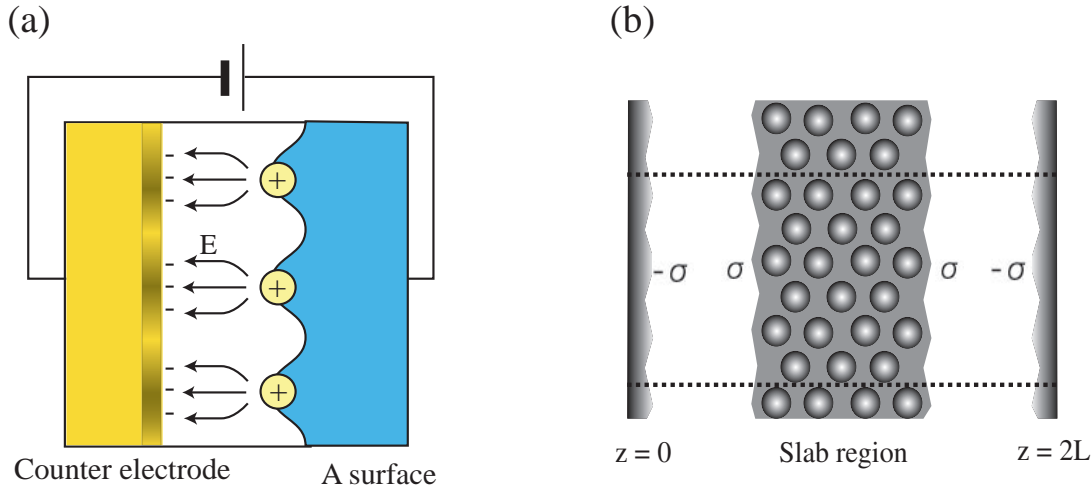


FIG. 1: (a) Schematic picture of charged surface system considered in this work. The surface and the counter electrode are connected with a cathode and an anode of an electric battery, respectively. Arrows denote an electronic field, \mathbf{E} , in the vacuum region. (b) A slab setup employed in the present calculation to simulate the charged surface shown in (a). The center of the slab is located at $z = L$ and each surface of the slab has a charge $+\sigma$. Two counter charged sheets are set at both boundaries and each electrode has the counter charge $-\sigma$.

charged surfaces located nearest to a constant-potential electrode by a standard *ab-initio* method based on the PBC. By only adding $\rho_F(k, \mathbf{g})$, we can obtain physical quantities such as the electron distribution, the electronic potential, forces on ions, and the total energy of the system composed of the charged surface with the counter electrode.¹⁷

III. RESULTS AND DISCUSSION

In this section, we demonstrate how the present scheme works. We consider a charged H_2 molecule, and charged Al(111) and Si(111) 1×1 surfaces. These systems are arranged at the center of a repeated unit cell and the atomic positions of all systems are optimized. We perform a standard *ab-initio* calculation based on the density functional theory (DFT)^{18,19} using a plane-wave basis set with an energy less than 25 Ryd. for the H_2 system and 16 Ryd. for the Al(111) and Si(111) systems. The present scheme is implemented into the computational code “Tokyo *ab-initio* program package” (Tapp).²⁰ The Perdew-Burke-Ernzerhof (PBE)²¹ functional in a generalized gradient approximation (GGA) is employed as an exchange-correlation potential for the H_2 system, while the Perdew-Wang²² functional in a local density approximation (LDA) is adopted for the Al(111) and Si(111) systems. The ionic cores are described by ultrasoft pseudopotentials²³ in all cases.

Figure 2(a) shows the setup of a H_2 molecule in a unit cell. Unit cells having $10.0 \times 10.0 \times 12.5$ and $10.0 \times 10.0 \times 18.75$ a.u.³ sizes are adopted. The H_2 molecule is surrounded by vacuum in all directions. The

counter charged sheets are set at unit cell boundaries of the z direction. We ionize this molecule positively as $\text{H}_2^{+0.1}$ by extracting 0.1 electrons. Figures 2(b) and 2(c) show the counter maps of induced charge density calculated at the cell boundaries, when the charged sheets are placed 5.5 and 8.7 a.u. apart from the nearest hydrogen atom of the molecule, respectively. In Fig. 2(c), since the distance between the molecule and the counter charged sheet is large, the electric field generated by the molecule uniformly touches the sheet and the charge distribution on the sheet becomes uniform. However, when the sheet approaches the molecule, reflecting the nonuniform charge distribution of $\text{H}_2^{+0.1}$, the induced charge shows a spacial modulation, as shown in Fig. 2(b).

Next, we consider positively charged Al(111) and Si(111) surfaces. Figures 3(a) and 3(b) show the excess-charge distributions of these systems viewed from the $[10\bar{1}]$ and $[1\bar{1}0]$ directions, respectively. Both surfaces are located about 10 a.u. from the counter electrodes. The excess-charge distribution is calculated as the difference in the charge density between charged and neutral systems. In the case of the Al(111) metal surface, since the electrons are weakly bound to atoms in metals, the excess charge is uniformly distributed along the surface. As a result, the counter charge on the sheet becomes uniform and parallel to the surface. On the other hand, in the case of the Si(111) surface, because dangling bonds have the highest energy in the surface, the inserted positive charge is mainly localized around dangling bonds of surface Si atoms. Thus, the counter charge on the sheet focuses at positions just above and below the dangling bonds.

Then, we consider how a constant zero potential is realized on the counter charged sheet. In the present

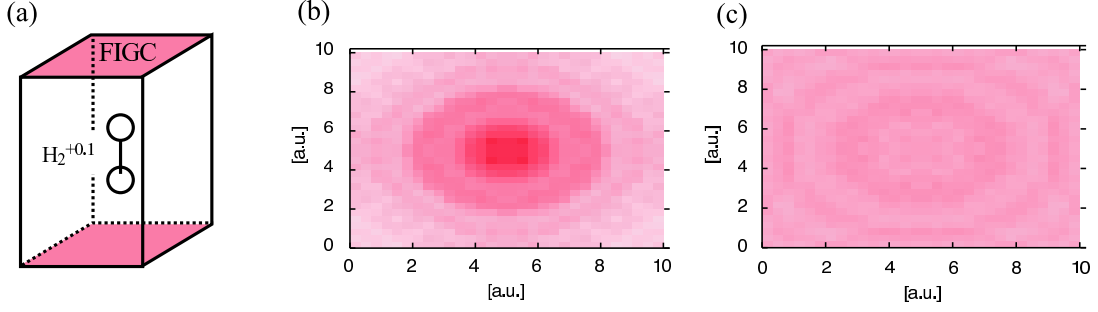


FIG. 2: (a); Schematic view of charged $\text{H}_2^{+0.1}$ molecule arranged in repeated unit cell. FIGC indicates the position of field-induced Gaussian-charge sheets, which are located at both the top and bottom of the cell. (b) and (c) are contour maps of charge distribution on the sheets when the sheets are located (b) 5.5 and (c) 8.7 a.u. from a nearest hydrogen atom. Denser color corresponds to higher density.

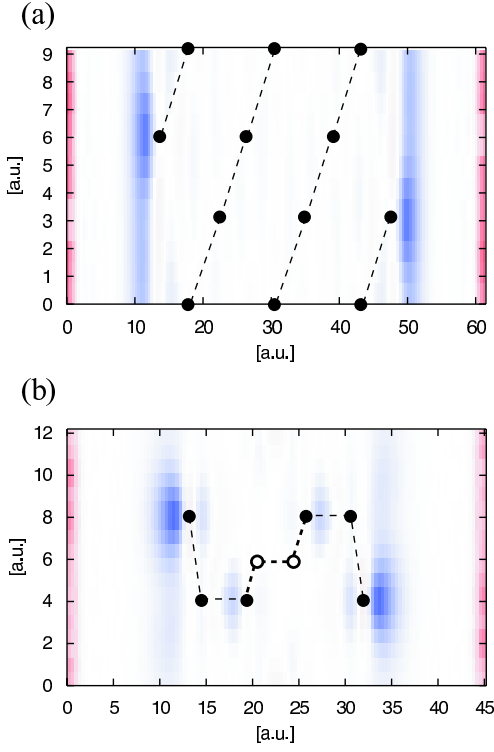


FIG. 3: Cross-sectional $[10\bar{1}]$ and $[1\bar{1}0]$ views of excess-charge distributions for (a) $\text{Al}^{+0.1}(111)$ and (b) $\text{Si}^{+0.1}(111)$ surface slabs. The charge distributions of the counter charged sheets are also shown. Blue and red areas correspond to positive and negative charges, respectively. Solid circles indicate atoms on the display plane, while open circles indicate atoms out of the plane. A Gaussian-charge width of $a = 1.0$ a.u. is adopted in both (a) and (b).

repeated-slab scheme, there exists one artificial parameter: the width of the Gaussian-charge sheet, denoted as a in eq. (3). This width is introduced to decrease the number of the plane-wave basis set and, thus, the computational time. However, owing to a finite a , the zero-potential condition assumed in the present method

is slightly released. This situation can be understood by observing the potentials on the sheet. The potential at $z = 0$ is, for example, obtained by the sum of the k -components of the total potential as $\phi(\mathbf{g}, z = 0) = \sum_{k=-\infty}^{\infty} \phi(\mathbf{g}, k)/2L$. Using a simple calculation, we obtain

$$\phi(\mathbf{g}, z = 0) = \frac{1}{2L} \sum_{k'=-\infty}^{\infty} \phi_{slb}(\mathbf{g}, k') \times \left\{ 1 - \frac{g}{L} \tanh(Lg) \sum_{k=-\infty}^{\infty} \frac{e^{-(\frac{ka}{2})^2}}{k^2 + g^2} \right\} \quad (6)$$

At $a = 0$, it can be analytically derived that the right hand of eq.(6) equals zero using the series formula $\sum_{n=-\infty}^{\infty} \frac{1}{X^2 + n^2} = \frac{\pi}{X \tanh(\pi X)}$, where X is an arbitrary real number and n is an integer. Hence, the zero-potential condition is satisfied on the sheet.

On the other hand, in the case of a finite a , we show in Fig. 4 the calculated $\phi(\mathbf{g}, z = 0)$ for the charged $\text{H}_2^{+0.1}$ system shown in Fig. 2(a). Here, the charged sheets are arranged 5.5 a.u. apart from the hydrogen molecule. The $\phi(\mathbf{g}, z = 0)$ values using the conventional fixed Gaussian-charge-sheet method are also shown for reference. This $\phi(\mathbf{g}, z = 0)$ represents the spacial modulation of potential on the counter charged sheets, corresponding to the wave vector \mathbf{g} . The result using the fixed Gaussian-charge sheet shows a potential modulation of about 20 meV, thus, not realizing the constant zero potential. On the other hand, in the case of the present scheme, it is seen that the potential modulation of each wave vector is suppressed and the potential modulation decreases with a . Therefore, a zero potential can be realized as long as a small a is employed.

IV. SUMMARY

To calculate the electronic structures of charged surfaces located near a flat and metallic counter electrode,

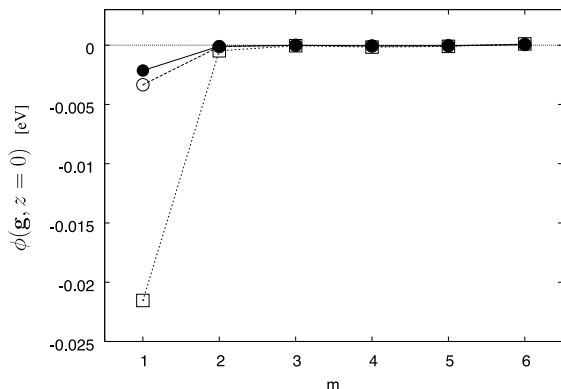


FIG. 4: Fourier components of total potential on counter charged sheet at $z = 0$, $\phi(\mathbf{g}, z = 0)$, for various in-plane wave vectors, \mathbf{g} . A charged $H_2^{+0.1}$ molecule is located at the center of a unit cell, 5.5 a.u. apart from the sheets. We adopt \mathbf{g} characterized by the an integer m , as $\mathbf{g} = g_0(m, m)$, where g_0 is the length of the in-plane fundamental reciprocal vector. Solid and open circles indicate the potential components obtained by the FIGC scheme using the widths $a = 0.3$ and $a = 0.5$ a.u., respectively, whereas open squares denote those obtained by the conventional fixed Gaussian-charge-sheet method using a width of $a = 0.5$ a.u..

we developed a new method that uses neutralizing variable charged sheets to realize a constant potential on the electrode. Since the present method is constructed on the basis of the PBC and a neutral unit cell, this method has the significant advantages that the implementation into existing repeated-slab programs is easy and the additional computational time is short. We have demonstrated that the present scheme works well not only for metal surfaces but also for semiconductor and insulator surfaces, and surfaces with adsorbates. We hope that the present scheme will be implemented in various programs and used for the study of charged surfaces.

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 - ¹⁶ See, for example, D. J. Griffiths: *Introduction to Electrodynamics* (Prentice Hall, New Jersey, 1999), 3rd ed., §2.5.
 - ¹⁷ There exists a constant electric field between a charged surface and a counter charged sheet, *i.e.*, in a vacuum region, and the energy of the electric field is stored in a vacuum region. Therefore, the total energy of the charged system depends on the position where we set the counter charged sheet in a vacuum region; namely, the position of the counter charged sheet is the energy origin of the total energy. One has to compare the energy stability of charged systems maintaining the position of the counter charged sheet. A precise discussion of the energy of a charged system is presented in ref. 13.
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